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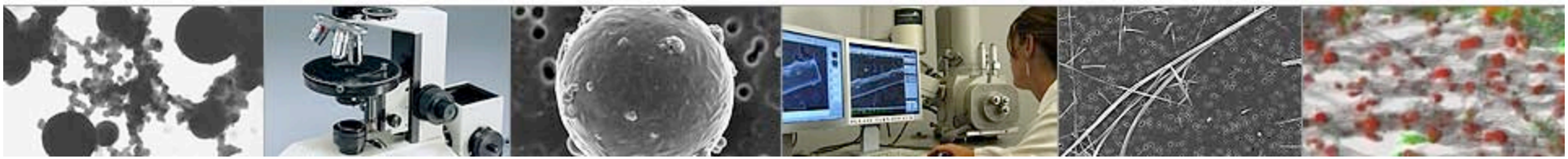
ES&H Challenges: Air Sampling and Analysis

Gary Casuccio

ES&H Challenges of the Nanotechnology Revolution

Lawrence Berkeley National Laboratory

July 29, 2009



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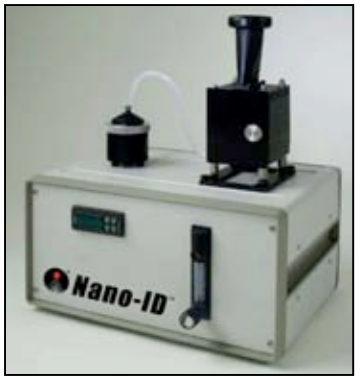
Sampling and Analysis Strategies









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The Promise of Nanotechnology

- Novel properties/ phenomena/ processes
  - Richard Feynman (1959)
    - "*There's Plenty of Room at the Bottom*"
- Could revolutionize science, technology, medicine and space exploration
- A new world of products:
  - Next economic engine?
    - >$2.5 trillion within next decade
    - ~ 2 million nanotech workers

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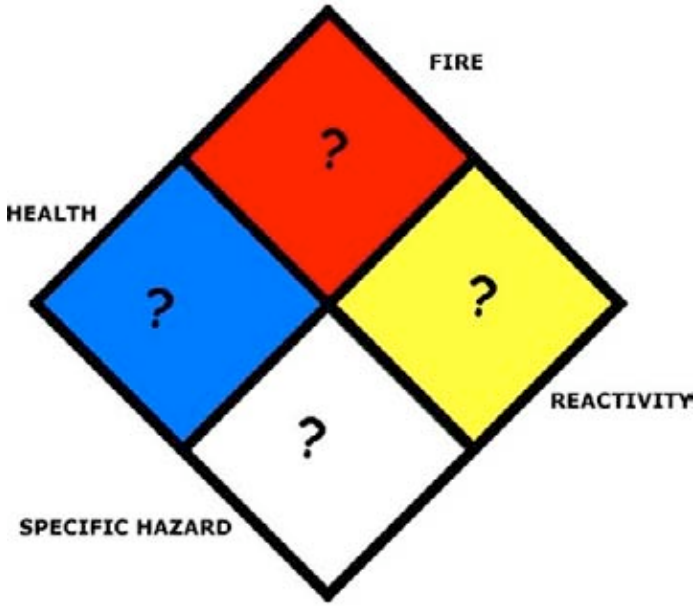
Issues Related to Engineered Nanoparticles

- Uncertainties
  - Short/Long Term Health Effects
- Societal Concerns
  - Environmental releases
  - Disposal
  - Intended use
- Analytical Issues
  - Sampling methodology
  - Analysis protocols
  - Standards



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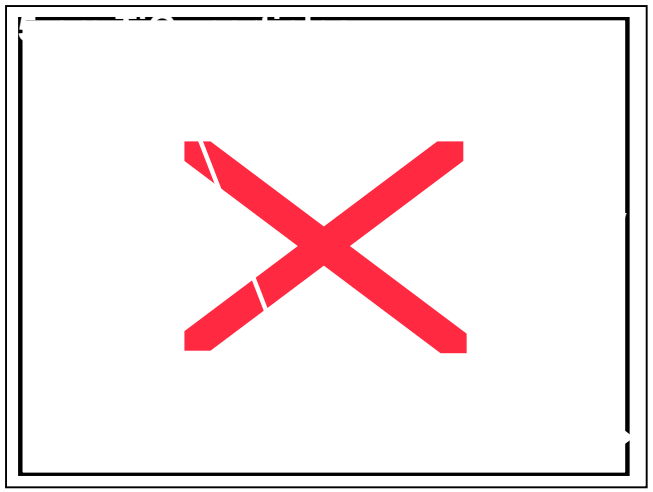
DOE Definition of Engineered Nanoparticle

- **engineered nanoparticle**, a particle intentionally created (in contrast with natural or incidentally formed) with **one** or more dimensions greater than 1 nanometer and less than 100 nanometers

- **unbound engineered nanoparticle (UNP),** engineered nanoparticles that are not contained within a matrix that would be expected to prevent the nanoparticles from being separately mobile and a potential source of exposure

- **nanostructure (Draft – RJLG),** a microscopic agglomerate, aggregate or matrix which contains individual particles that are less than 100 nm in one or more dimensions



U.S. DOE N456.1: The Safe Handling of Unbound Engineered Nanoparticles, January 5, 2009

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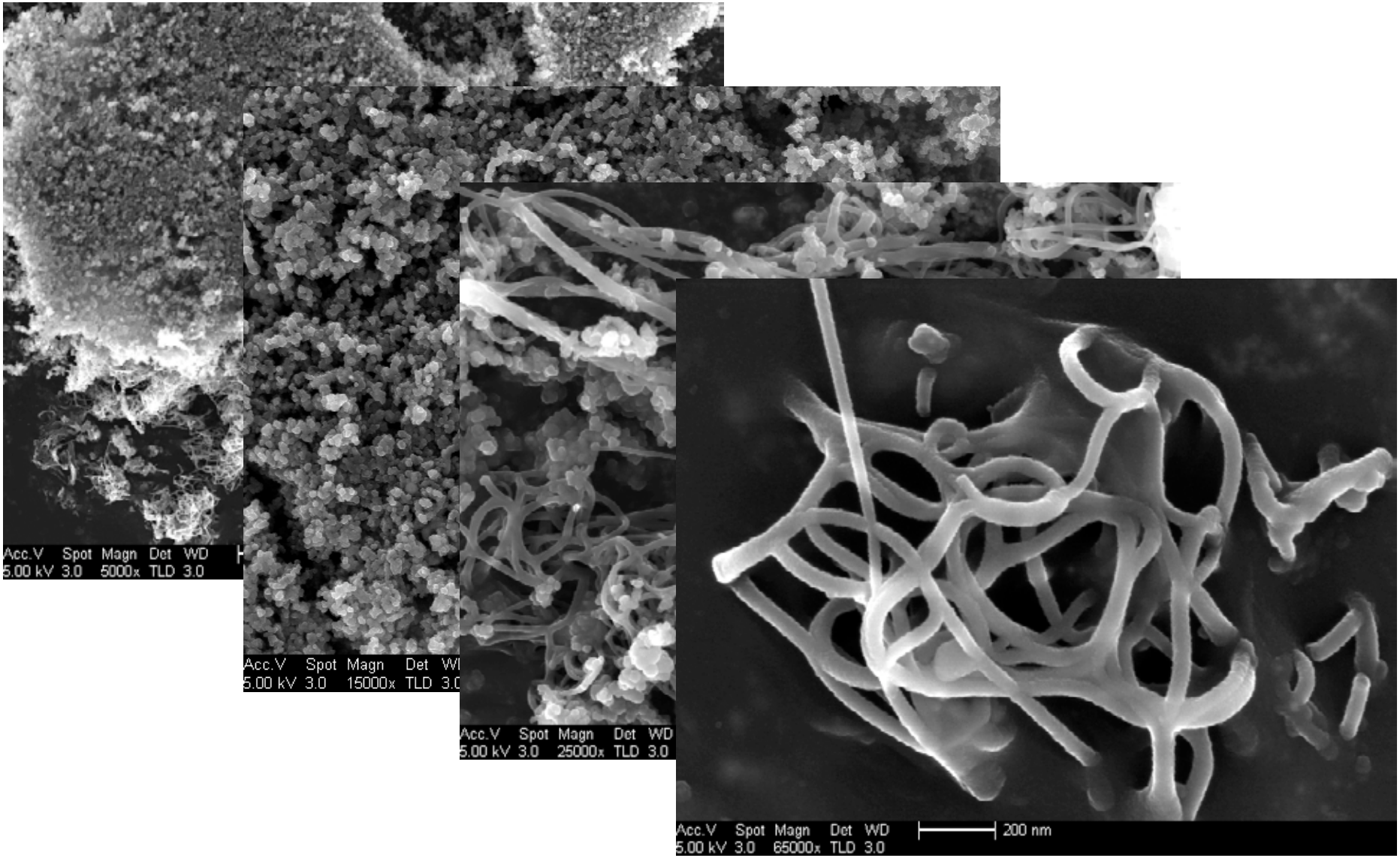
A Matter of Scale



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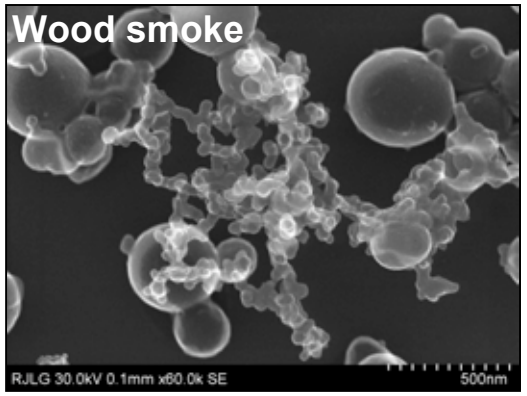
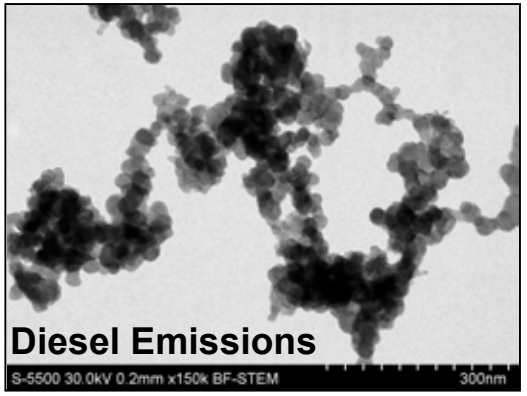
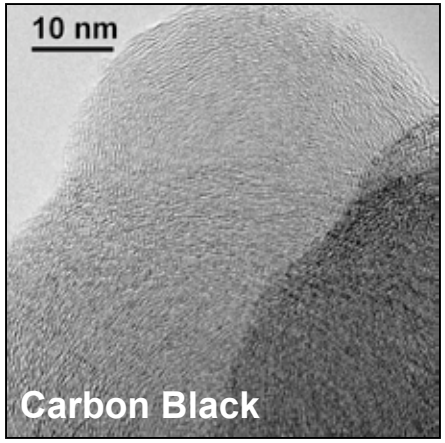
Nanoparticles are not new…

- Nanoparticles are all around us
  - ~10^6 nanoparticles per breath
- Natural and anthropogenic origins
  - Naturally occurring
    - Asbestos, volcanic ash, forest fire smoke, biological structures
  - Combustion (incidental) particles
    - Soot, metal oxides, welding fumes, diesel emissions
  - Historical engineered nanoparticles
    - Pigments, carbon black







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Sampling for Nanoparticles in the Workplace Environment

- Follow recommendations in Guidance Documents
  - DOE Approach Document[1]
  - NIOSH Approaches to Safe Nanotechnology
  - Process specific evaluation
    - Characterize the “source” and establish a source signature
    - Compare signature to particles collected on worker exposure or environmental samples

[1]Department of Energy Nanoscale Science Research Centers: Approach to Nanomaterial Environmental Safety & Health, Office of Science, U.S. Department of Energy, NSRC Revision 3a, May, 2008.

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Sampling for Nanoparticles in the Workplace Environment

- Learn from previous experiences
  - "If we don't pay attention to the past, we are likely to make the same mistakes in the future."
  - The asbestos experience
  - Single crystal ceramic whiskers
- Base initial nanoparticle sampling and analysis protocols on established methodologies
  - Modify as new information becomes available
  - Realize that this is an evolutionary process

How do we evaluate nanoparticles?

- In an ideal world,
  - we would have field deployable tools that would acquire data on individual nanoparticles (size, morphology, composition and concentration) in real time

- In the real world,
  - use tools available today and develop methodologies that can be modified as new tools become available
    - Real time particle counters
    - Microscopy
    - Bulk analytical methods (gravimetry, ICP, etc.)
    - Surface area

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What are the measurement issues?

- Sampling and analysis protocols are developing
- Nanoparticle measurement is evolving
  - Direct-read instruments
  - Size selective sampling
  - Filter-based methods
- New analytical technology is available
- Can these new sampling and analysis technologies be used in a cost effective manner?

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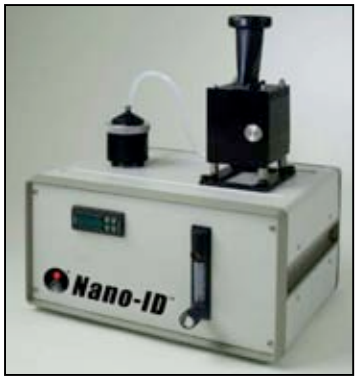
Sampling and Analysis Strategies









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Graded Approach to Aerosol Characterization

Level 1	Level 2	Level 3
Initial Screening and Detection	**Comprehensive Characterization and Assessment**	**Routine Monitoring and Control**
➢ Process knowledge ➢ Gross mass or activity counting ➢ Optical particle counting ➢ Condensation particle counting ➢ Microscopy	➢ Elemental composition ➢ Chemical composition ➢ Particle size - Physical - Aerodynamic - Thermodynamic - Electrical mobility ➢ Morphology ➢ Surface area ➢ Biological solubility ➢ Etc.	➢ A necessary and sufficient subset of Level 1 and 2 methods for the material and situation of interest

Hoover 2009 (draft)

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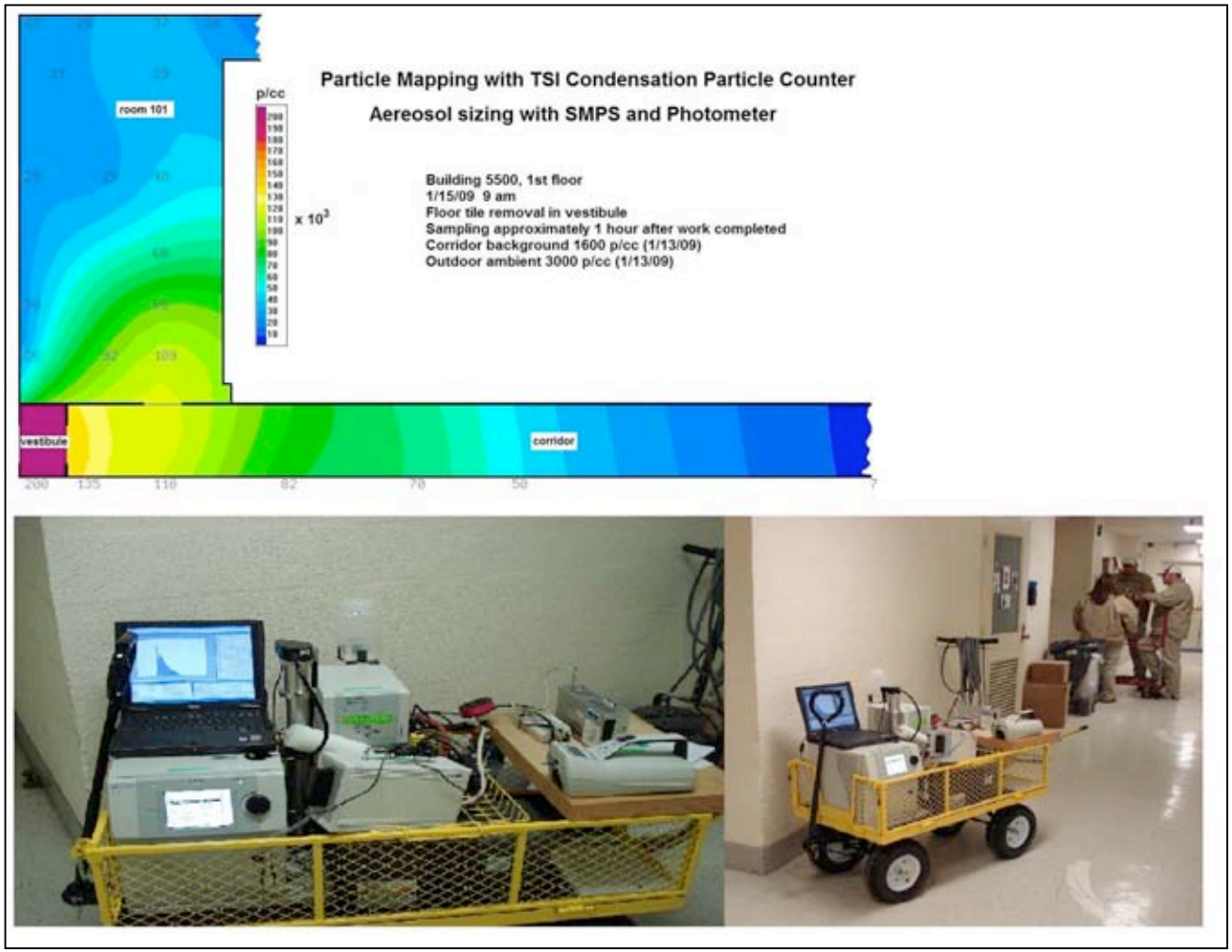
Nanoparticle Sampling at ORNL



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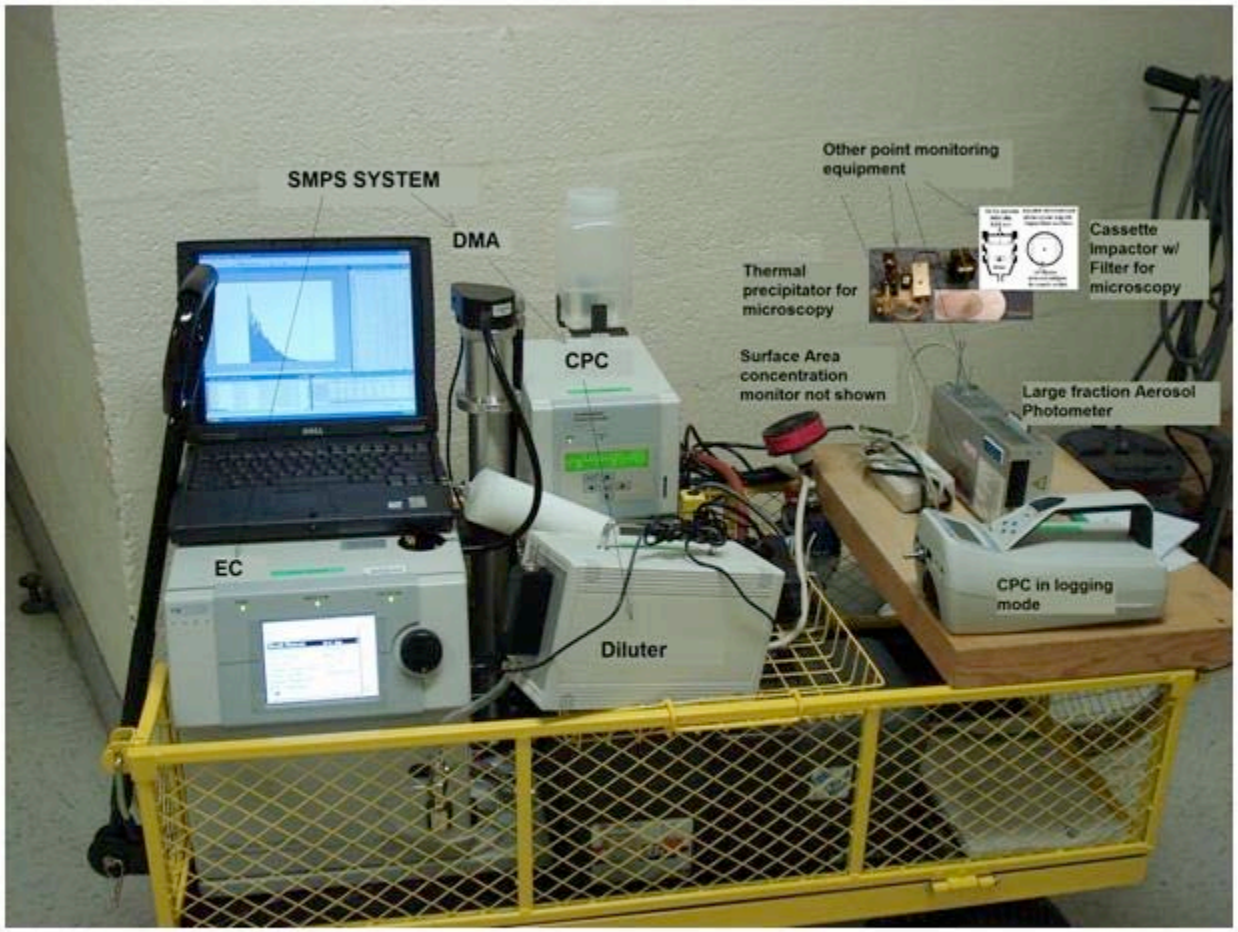
Nanoparticle Sampling at ORNL



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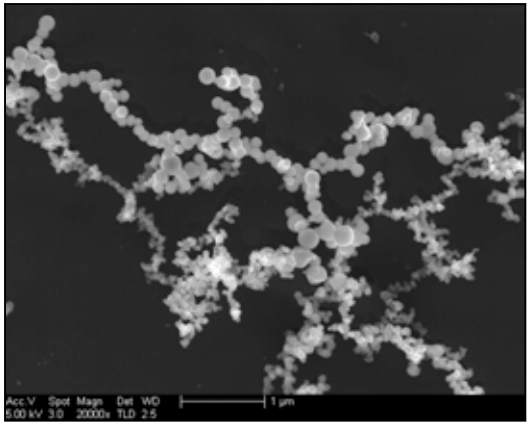
RJLG's phased approach to microscopy sample analysis

- Level I: Screening analysis provides basic information on sample characteristics
- Level II: More detailed analysis on size, morphology and chemical characteristics
- Level III: In-depth research analysis



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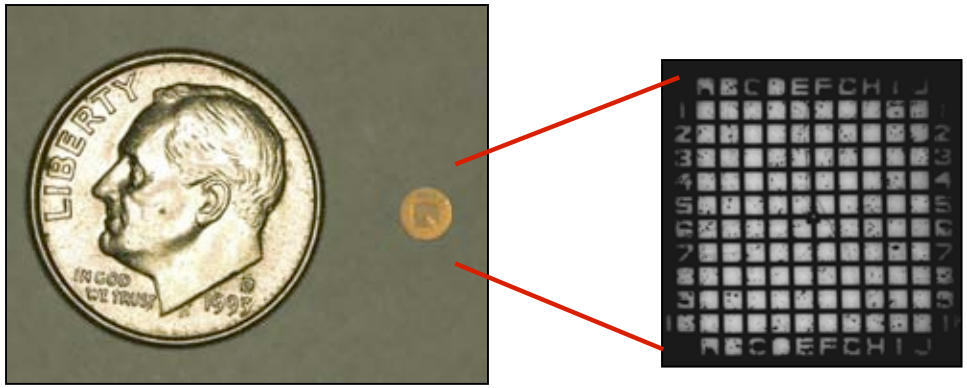
RJLG's Level I Microscopy Screening:

- Basic information regarding sample characteristics
  - Evaluate particle loading and general sample characteristics, including images and spectra of representative particles
  - Determination of which subset of samples will proceed to the Level II analysis



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RJLG's Level II Microscopy Analysis:

- Describe obvious morphological characteristics of the nanoparticle/nanostructure (spherical, elongated, aciniform, surface characteristics)
- Predominant size range of nanoparticles (agglomerates or individual particles)
- Elemental analysis to provide composition of representative particles
- Estimate of nanoparticle/nanostructure concentration for worker exposure samples (#/cc)

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RJLG's Level III Microscopy Analysis: R&D

- Larger population of particles analyzed
- Size distribution of the particles
- Determine if particles have homogenous or heterogeneous compositions
  - Bright Field/Z-Contrast imaging
  - Spectral imaging
- Evaluate surface coatings
  - Surface analysis techniques

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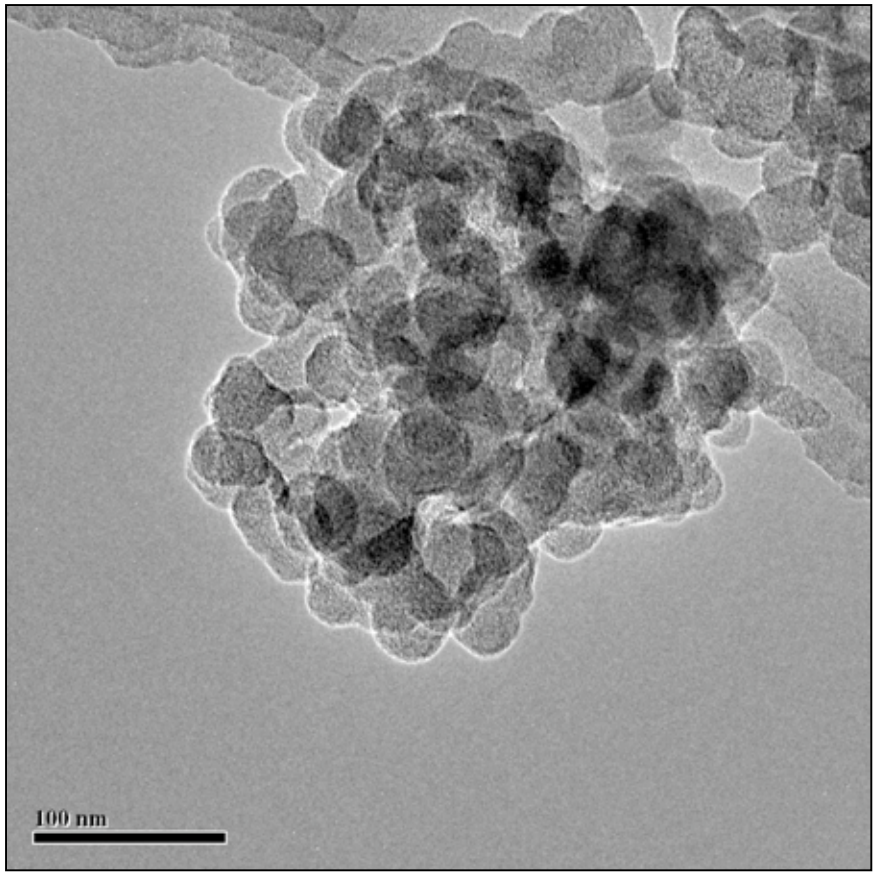
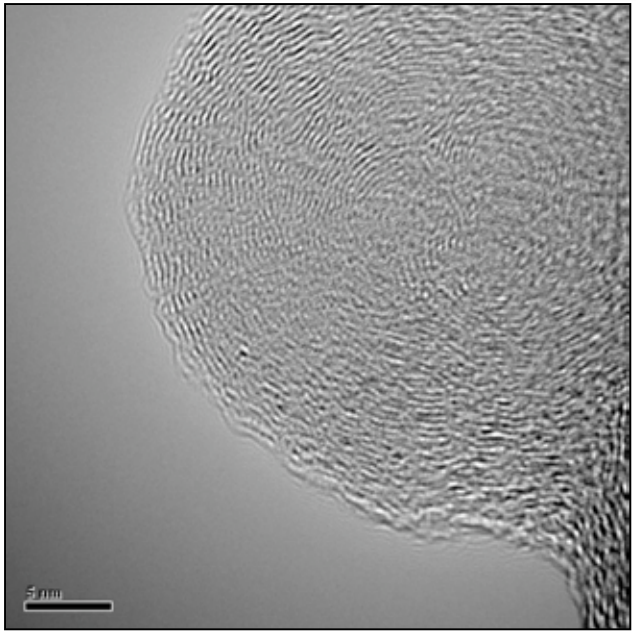
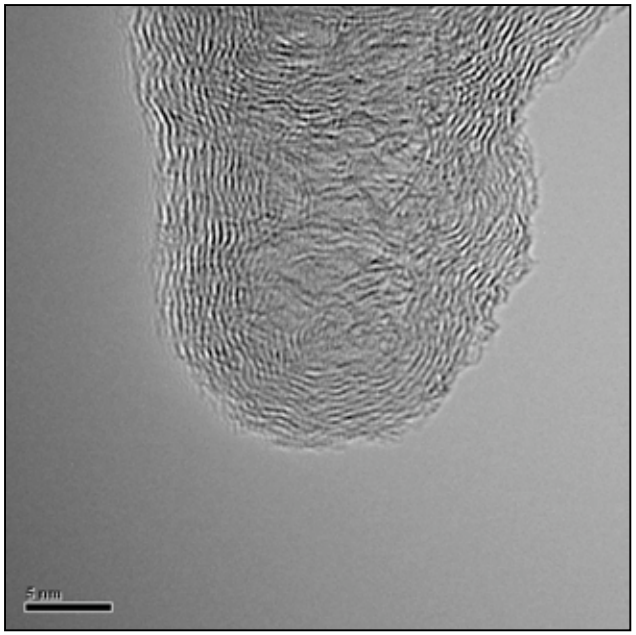
HR-FE-TEM Images of Carbon Black







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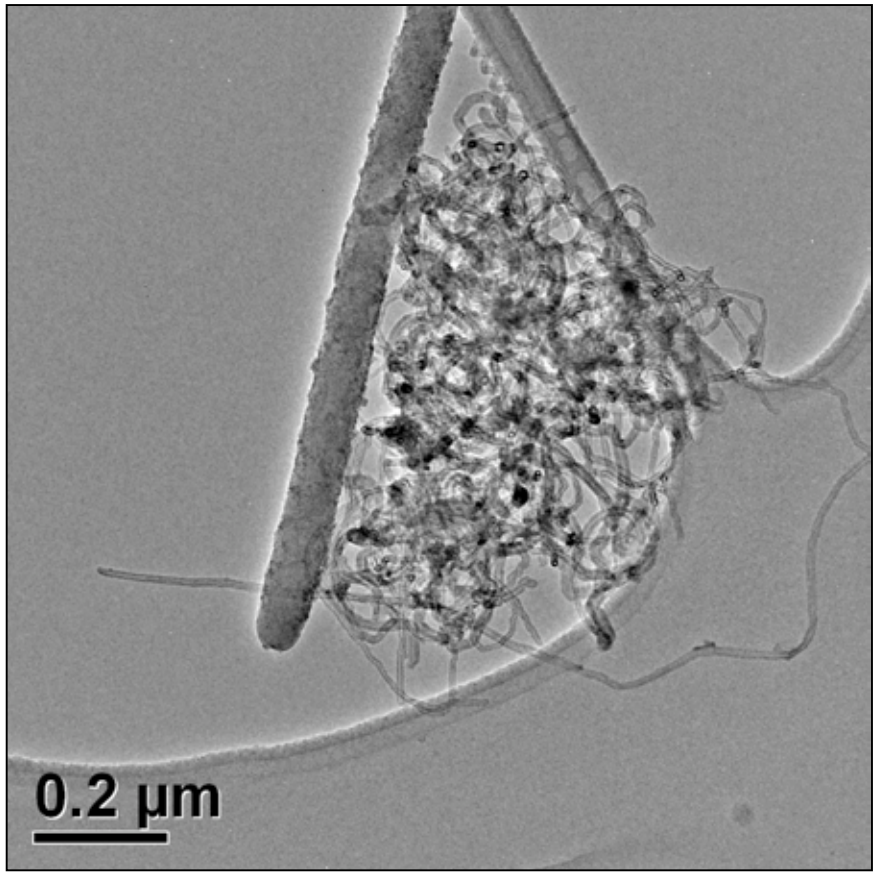
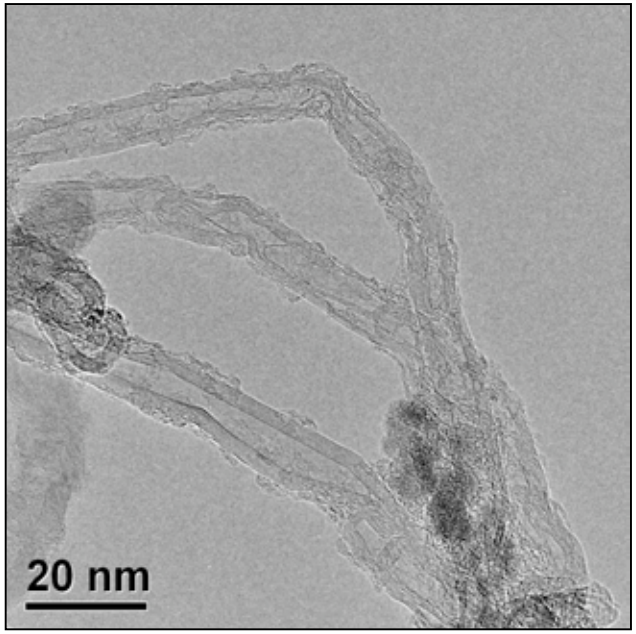
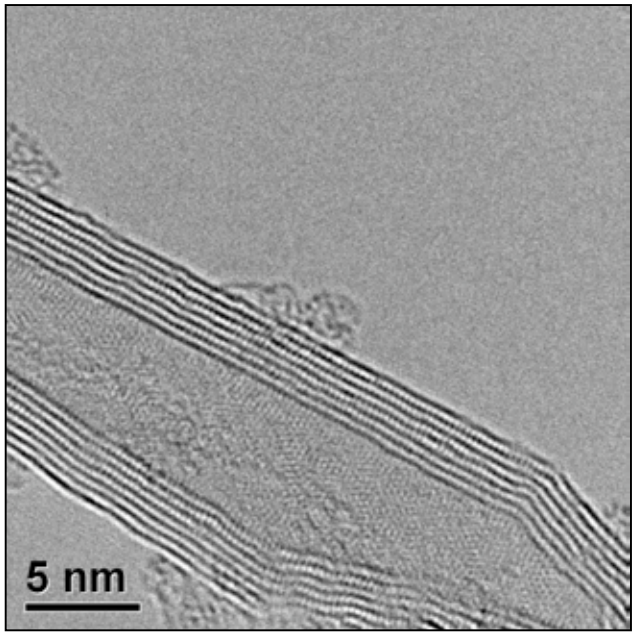
HRTEM







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Advances in Electron Microscopy: High-Resolution FESEM/STEM

Silicon Drift Detector for Elemental Analysis

- 30 kV cold field emission
- Magnifications up to 2,000,000X
- Secondary electron imaging
- Bright field and Z-contrast imaging
- Energy dispersive X-ray spectroscopy (EDS)
- Switch between all operation modes without changing the specimen position (including EDS)
- Change accelerating voltages easily

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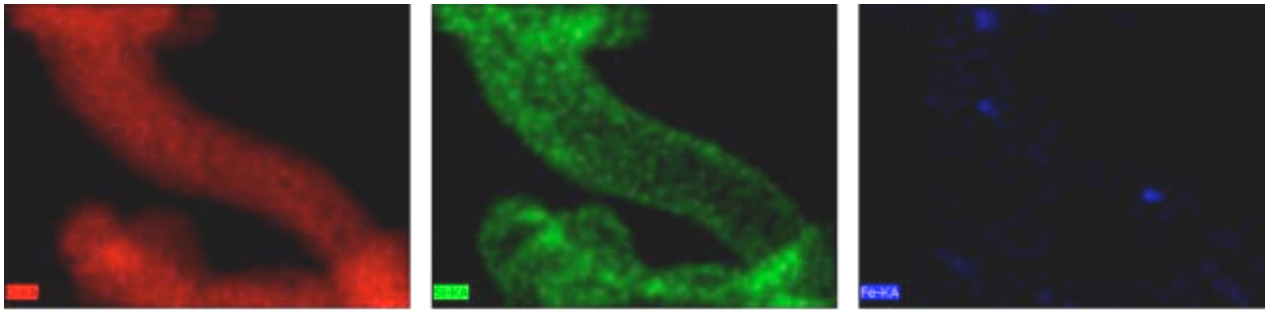
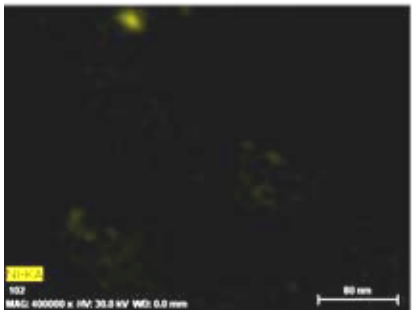
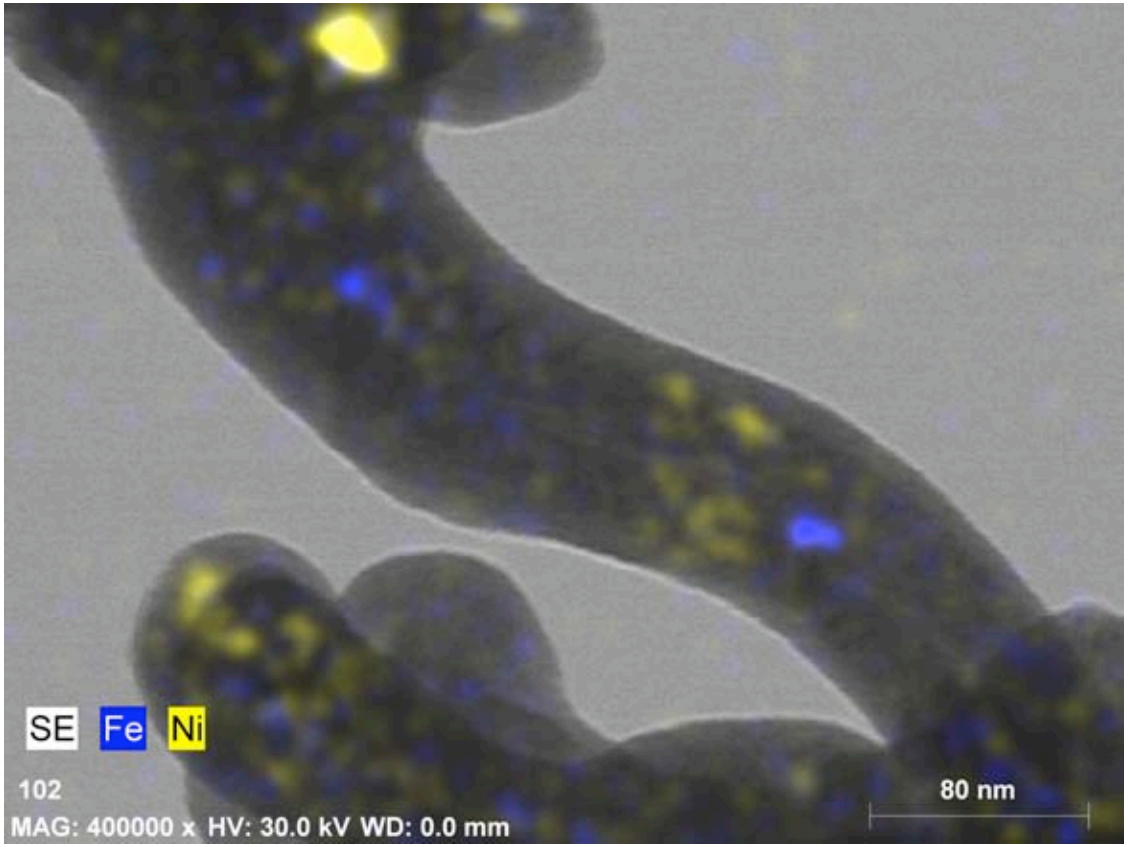
Bulk/Source Sample X-ray Map







Draft

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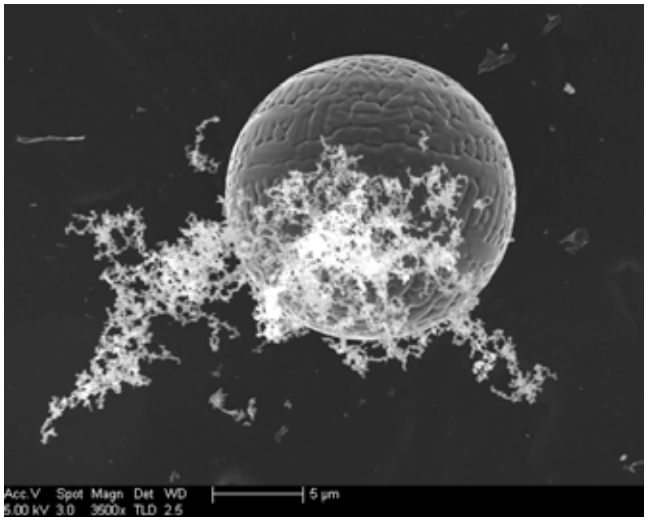
Case Study

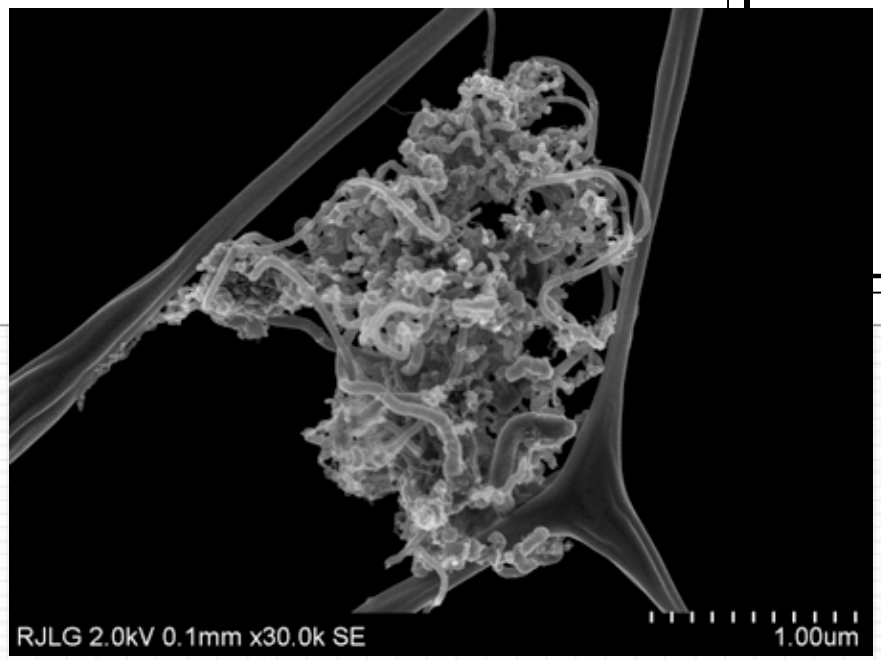
- Are nanoparticles/nanostructures on the workplace filter sample?
- Do the particles on the sample match a source material (size, morphology, chemistry)?
- What is the concentration (#/cc)?

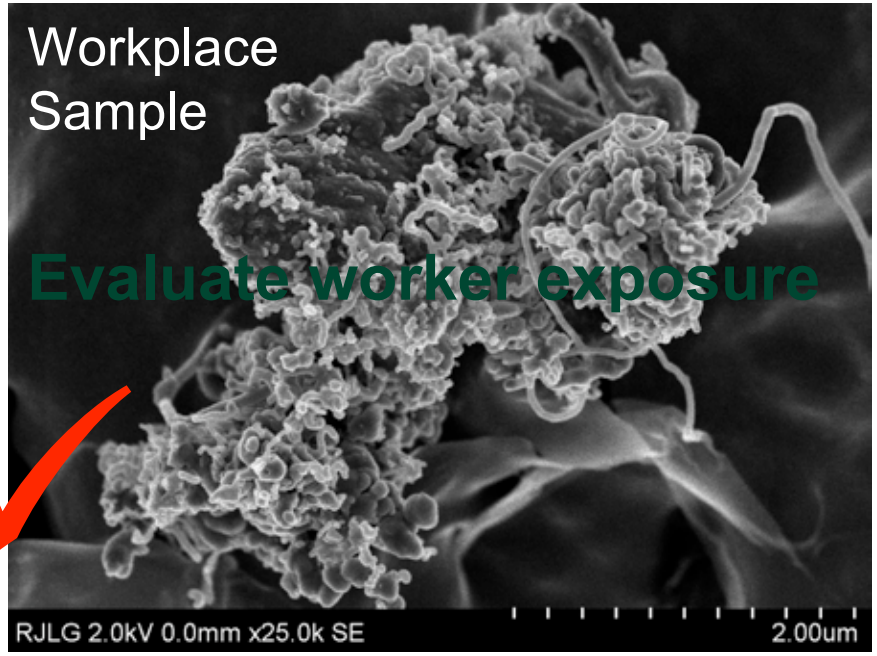


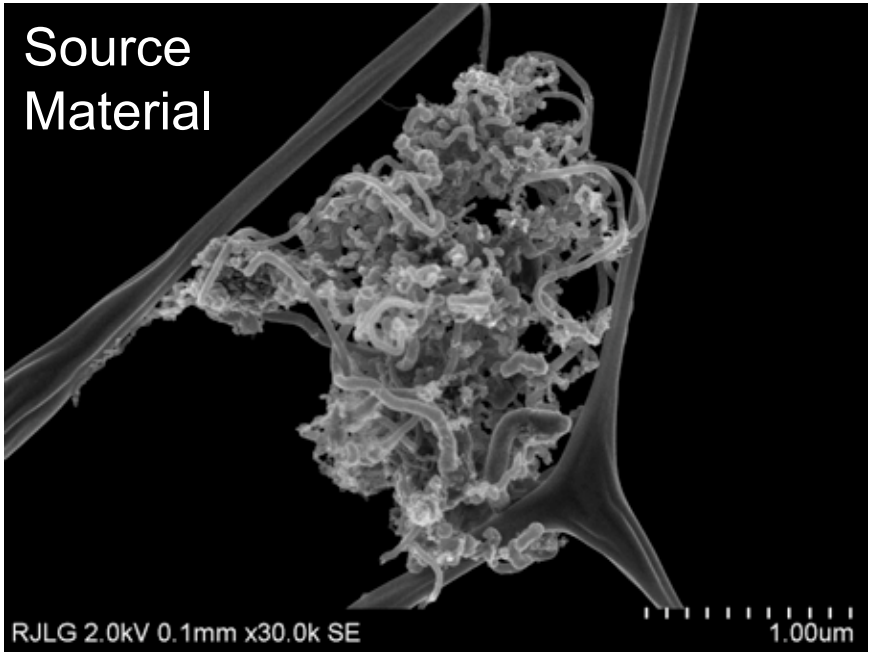
Analytical Approach

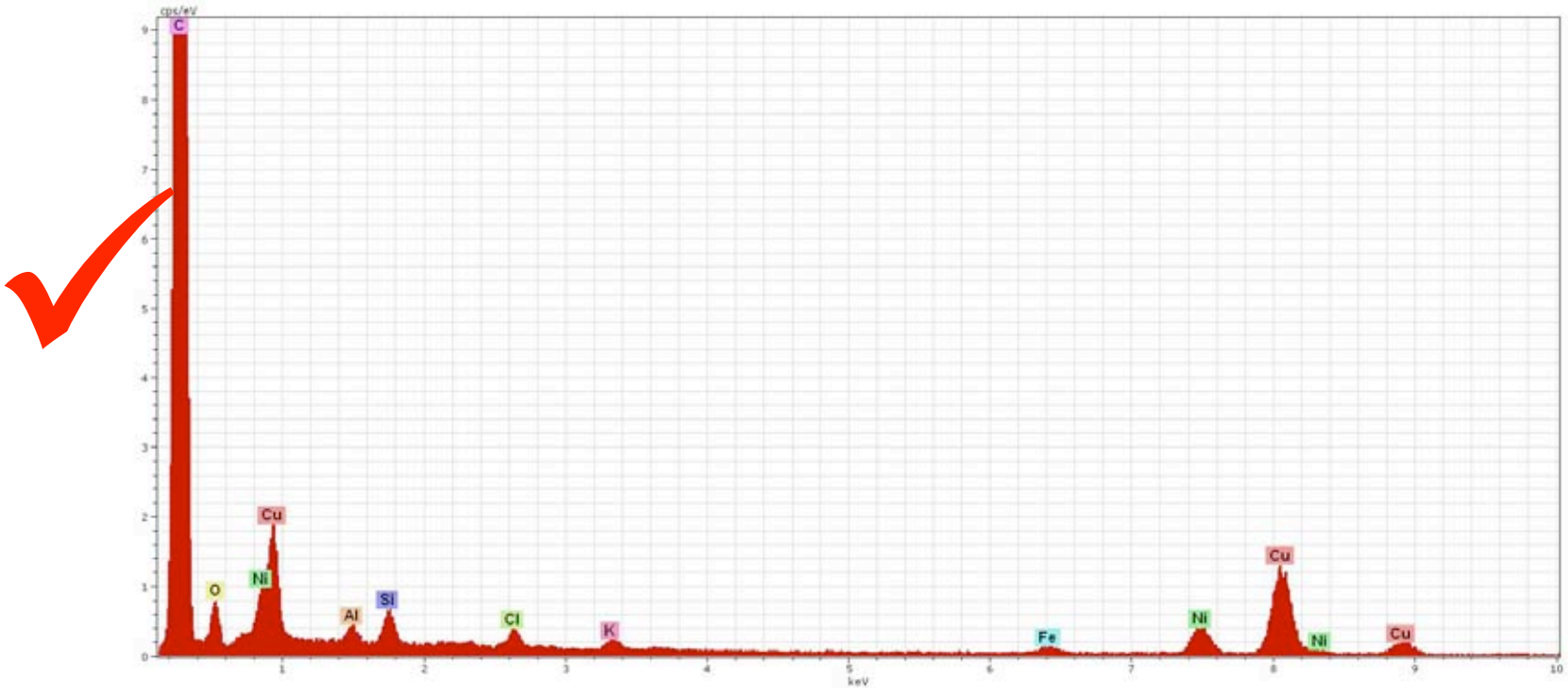
- Characterize “source” sample using Level II protocol
  - Define source signature
  - Source material should be representative of the process
- Examine workplace samples initially using Level I protocol
  - Compare to source and background samples
- Select sample(s) for Level II protocol

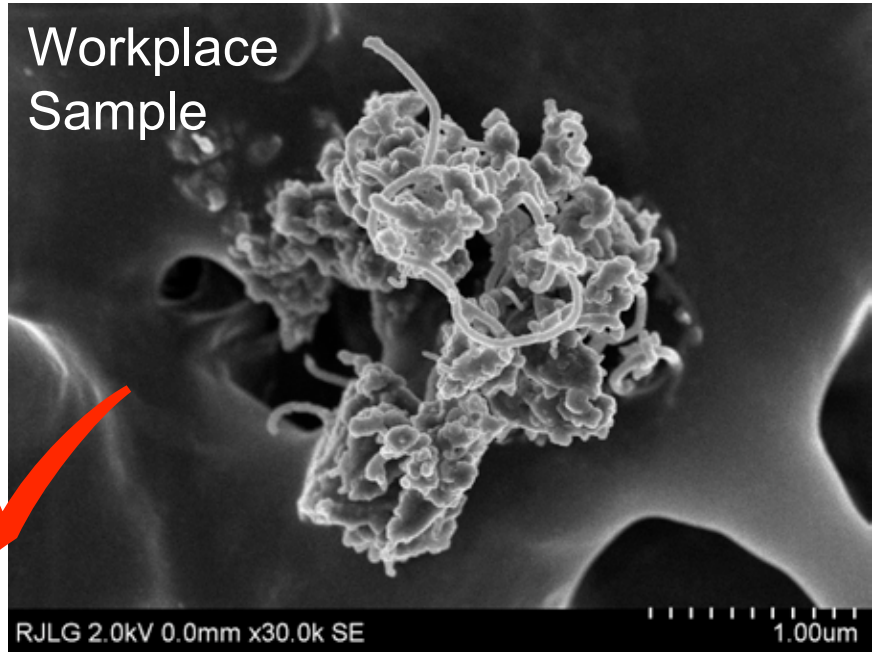
Establish Source Signature

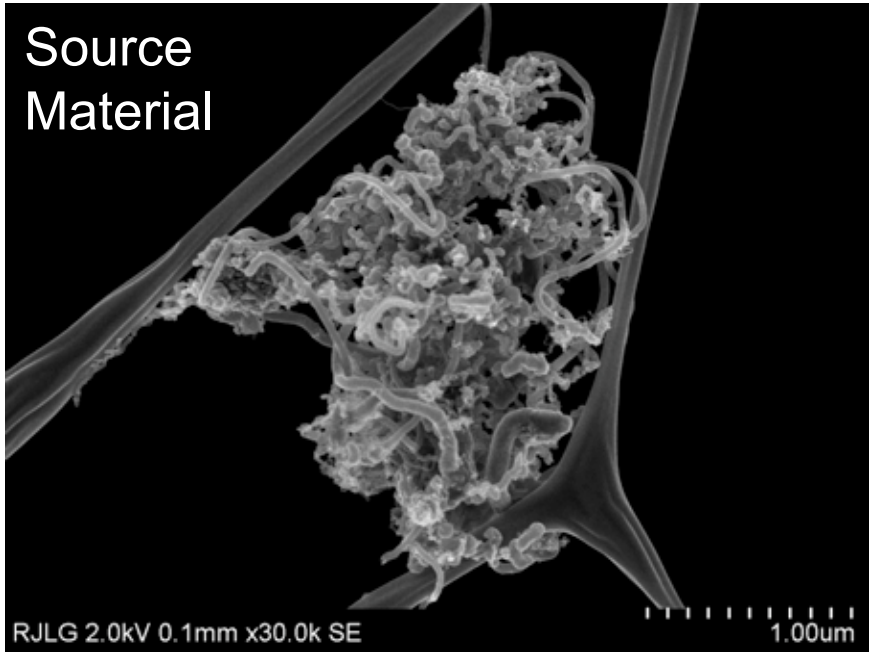


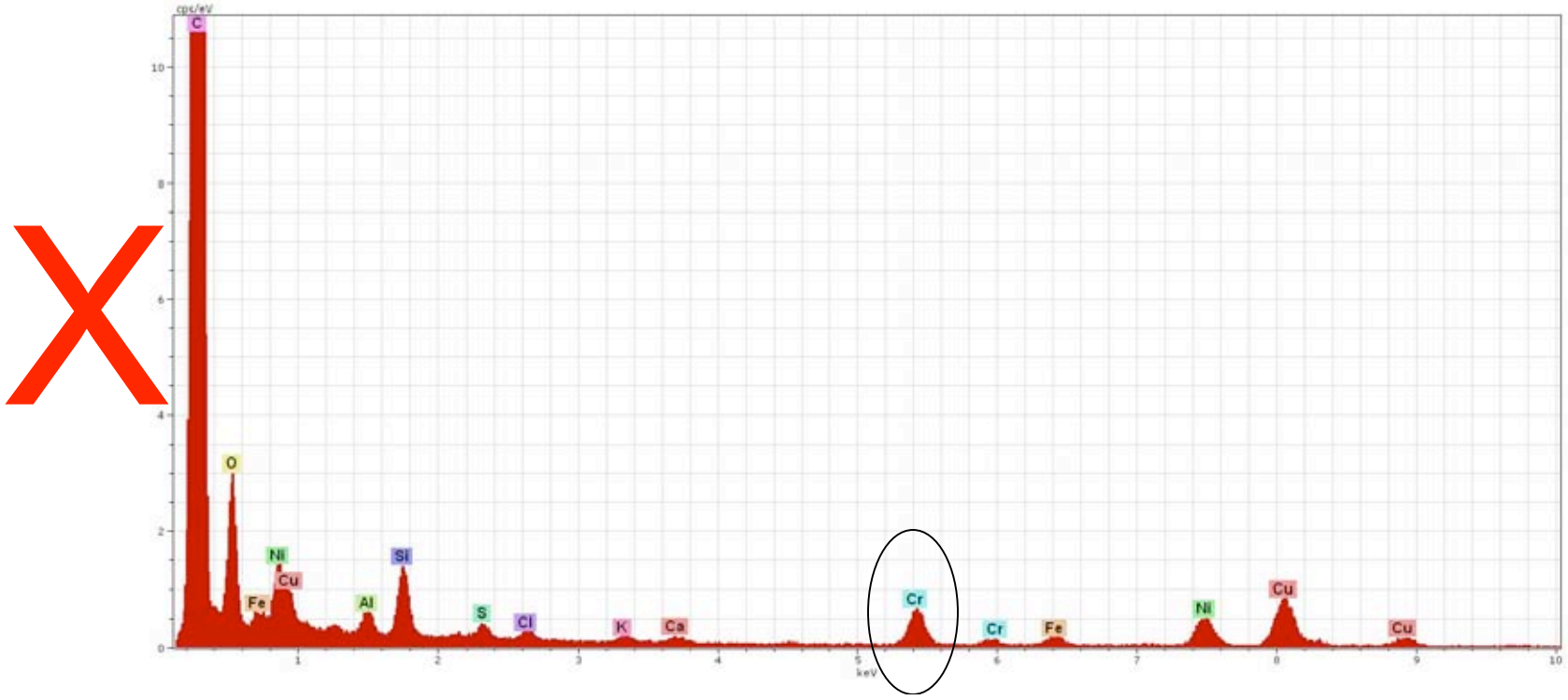

Workplace
Sample
Evaluate worker exposure
RJLG 2.0kV 0.0mm x25.0k SE
2.00um

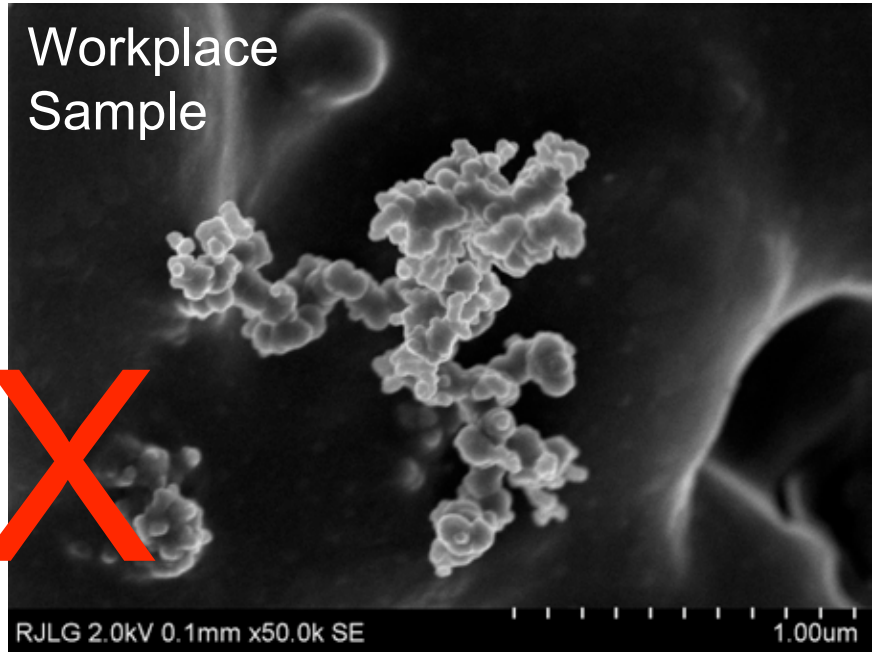

Source
Material
RJLG 2.0kV 0.1mm x30.0k SE
1.00um

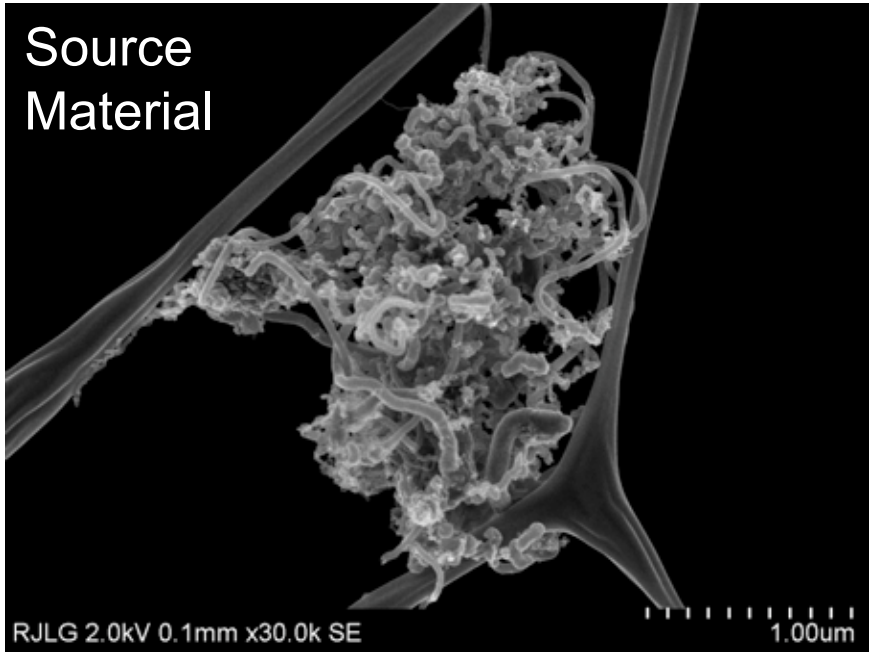

cps/eV
C
O
Ni
Cu
Al
Si
Cl
K
Fe
Ni
Cu
Ni
Cu
keV

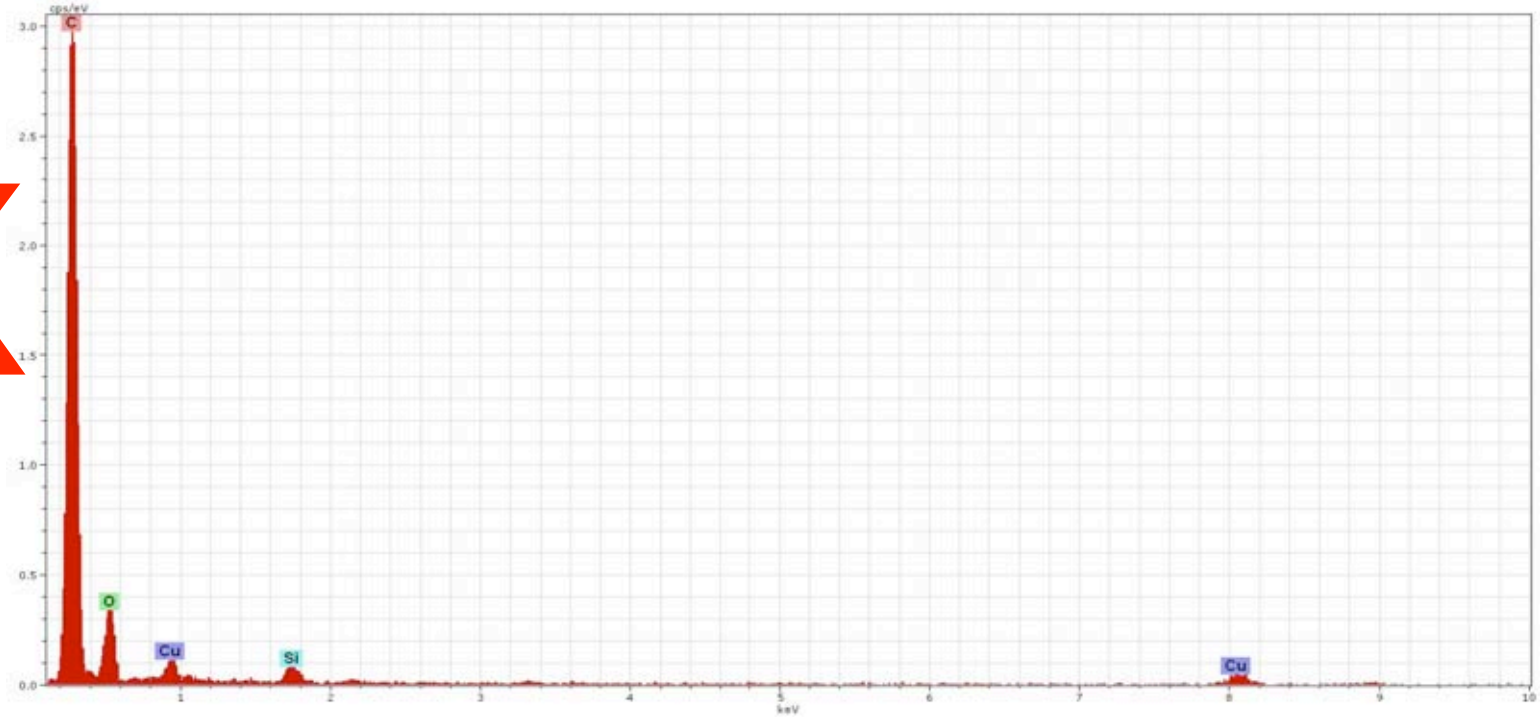

Workplace
Sample
RJLG 2.0kV 0.0mm x30.0k SE
1.00um


Source
Material
RJLG 2.0kV 0.1mm x30.0k SE
1.00um


cps/eV
C
O
Ni
Cu
Fe
Al
Si
S
Cl
K
Ca
Cr
Cr
Fe
Ni
Cu
Cu
keV


Workplace
Sample
RJLG 2.0kV 0.1mm x50.0k SE
1.00um


Source
Material
RJLG 2.0kV 0.1mm x30.0k SE
1.00um


cps/eV
C
O
Cu
Si
Cu
keV

Case Study Results

- Nanostructures consistent with the source material accounted for ~0.3 particles/cc
- Nanoparticles/nanostructures not consistent with the source material accounted for ~40 particles/cc

Implications

- Other source(s) of nanopartices or bulk source material may not be representative of all nanoparticle/nanostructures emitted from the source

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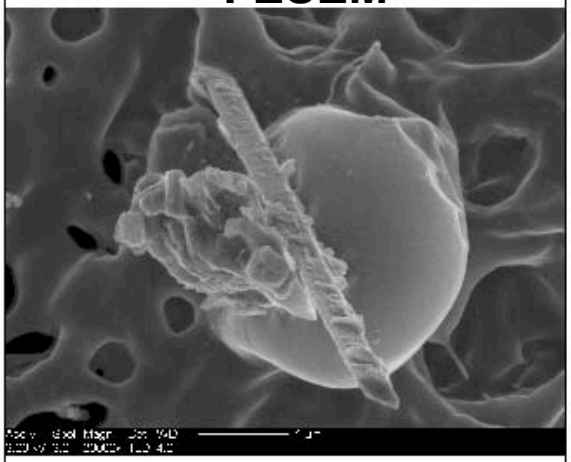
Particle Classification Database

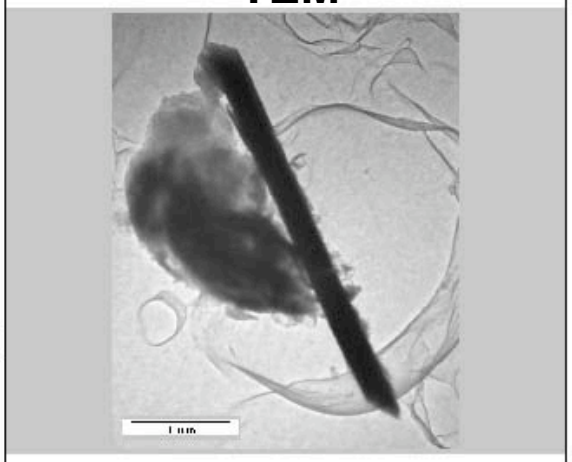
SEM Note:
TEM Note:

FESEM



Set First Fiber

TEM



Shapes	☐ Acicular	☒ Prismatic	☐ Bladed	☐ Columnar	☐ Layered	☐ Fiber	☐ Curvature	☐ Bundle	☐ Irregular	☐ NA	
Surface	☐ Smooth	☐ Textured	☒ Rough	☐ Mottled	☐ Steps	☐ Striations	☐ Embedded	☐ Coated	☐ Superstructure	☐ NA	
Sides	☒ Parallel	☐ NonParallel	☐ Tapered	☐ Irregular	☐ Stepped	☒ Rough	☐ NA				
Ends	☐ Blunt	☒ Perpendicular	☐ Angled	☐ Irregular	☐ Stepped	☐ Needle-like	☐ Tapered	☐ Splayed	☐ NA		
Association	☐ Anchored	☒ Coherent	☒ Contact	☐ Free Standing	☐ NA						
Part.Relation to Filter	☐ Flat	☐ Upright	☒ Inclined	☐ Suspended	☒ Supported	☐ NA					

L = 4 W = .25 AR = 16:1

Final Call	☐ Asbestos	☒ Non-Asbestos
Damaged	☐	
Comment	Non-asbestiform richterite particle	

RJLG # 3045299.HT Field 28, Fiber 6

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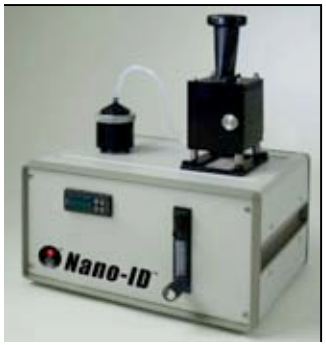
Proposed Sampling Strategies

- Combination of real time particle counters and filter based methods
  - Condensation particle counters
  - Microscopy
  - Bulk analytical methods (gravimetry, ICP, etc.)
- Looking to the future
  - Evaluate samplers that can collect samples directly on TEM grids
  - Explore potential to develop samplers that can integrate real time data with collection of samples of interest



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A Pilot Study of UNP at LBNL

- Phase 1: Understand research through interviews, demonstrations, analysis of raw materials
- Phase 2: Develop preliminary control bands
  - List of potential hazards and ways to control them
- Phase 3: Validate and modify control bands
    - Sampling and Analysis
      - Personal exposure
      - Environment
      - Finalize Control Bands
- Phase 4: Develop ongoing monitoring plan

Summary

- Advanced analytical tools are available for the characterization of nanoparticles
  - Use these tools in a cost-effective manner
- Learn from previous experiences
- Sample in a “smart” manner
- Automate the process where possible
- Incorporate information in databases
- Sampling and analysis protocols are evolving and will continue to evolve as more information becomes available